BISMUTH AMALGAM - PHOSPHATE SELECTIVE ELECTRODE

By

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SELECTIVE ELECTRODE

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PREFACE

The objectives of this study were to construct and evaluate an ion selective electrode for orthophosphate.

Dr. Louis P. Varga served as major adviser. The other members of the advisory committee include Drs. Tom E. Moore, E. J. Eisenbraun, and Troy C. Dorris. I am grateful for the kind assistance of these and many other faculty members and colleagues.

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CHAPTER I

INTRODUCTION

Water pollution characterization is one of the most challenging tasks confronting the analyst. Physicochemical and biochemical transformations in aquatic environments must take into account interactions between the atmosphere, hydrosphere and lithosphere as depicted in Figure 1 (1).

Three basic nutrients, carbon, nitrogen and phosphorus, greatly influence aquatic biota. Eutrophication causes changes in plant and animal life that may interfere with use of the water, detract from natural beauty and reduce property values. One common result is excessive growth of algae and larger aquatic plants. Such growth chokes open water, makes it nonpotable and increases the cost of filtration. The decomposition of excess vegetation fouls the air, adds obnoxious taste to the water, and consumes deep-water oxygen vital for fish and other forms of life.

The limiting nutrient in the eutrophication process is not the same in all bodies of water. Many studies show that different nutrients may be limiting in the same water at different times. However, McGauhey (2) describes one popular view of nutrients in the following manner:

> It is generally conceded today that phosphorus is more important than nitrogen in causing algal blooms. In fact, an algal bloom may result from excess phosphate out of scale with the normal ratio of nitrogen to phosphorus in plant growth. This is the result of the development of types of algae which can fix nitrogen from the atmosphere provided there is plenty of available phosphate.

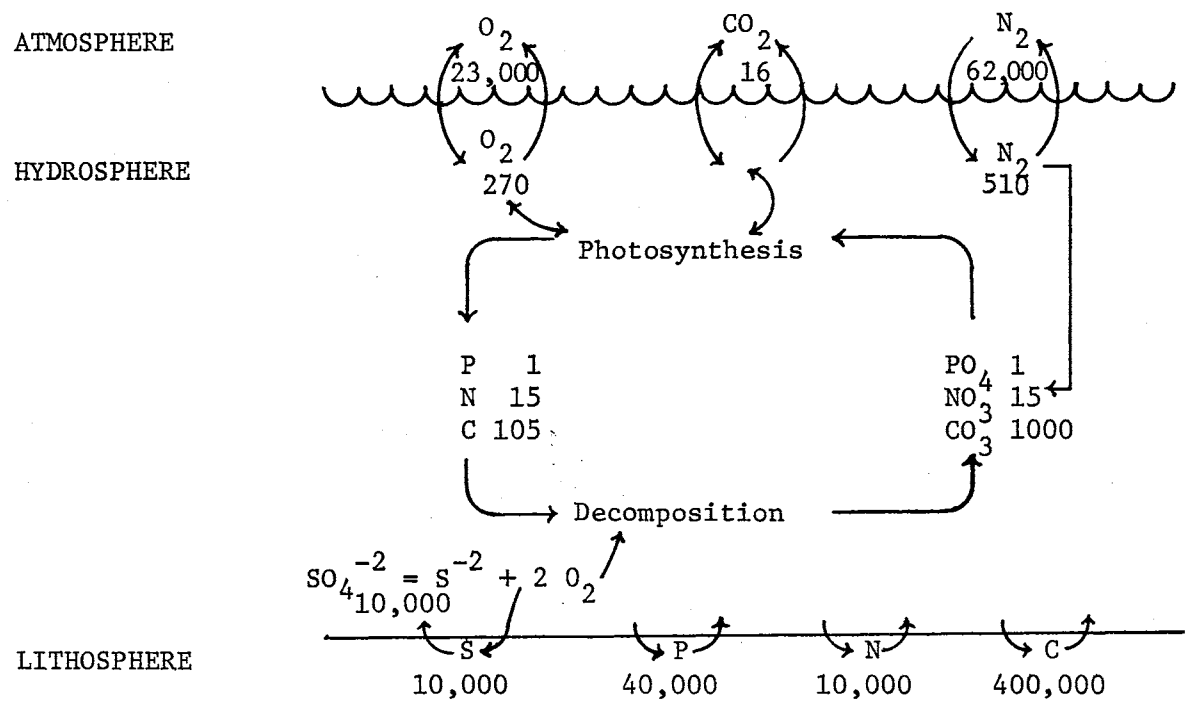

Figure 1. Interactions Between the Atmosphere, Hydrosphere and Lithosphere of Some Major Elements in Aquatic Ecosystems. The Ratios are Based on the Number of Atoms of the Designated Element Per Atom of Phosphorus (1)

Furthermore, statistics show that man is responsible for increasing phosphorus levels to a greater extent than nitrogen levels, Table I (3).

The complete characterization of natural water systems requires a large volume of detailed data. These data can not be practically obtained via the basis of grab sampling with subsequent laboratory analysis. Rapid and reliable, on-site continuous monitors are needed to provide information over extended periods of time. This information could be used to evaluate future changes in water quality, devise quality indices and set pollution standards.

The objective of this investigation is to develop and evaluate an ion selective electrode for the determination of orthophosphate in aqueous solutions.

TABLE I

SUMMARY OF ESTIMATED NITROGEN AND PHOSPHORUS REACHING WISCONSIN SURFACE WATERS (3)

Source	N	P	N	P
	Lbs. per year		(% of total)	
Municipal treatment facilities	20,000,000	7,000,000	24.5	55.7
Private sewage systems	4,800,000	280,000	5.9	2.2
Industrial wastes*	1,500,000	100,000	1.8	0.8
Rural sources				
Manured lands	8,110,000	2,700,000	9.9	21.5
Other cropland	576,000	384,000	0.7	3.1
Forest land	435,000	43,500	0.5	0.3
Pasture, woodlot & other lands	540,000	360,000	0.7	2.9
Ground water	34,300,000	285,000	42.0	2.3
Urban runoff	4,450,000	1,250,000	5.5	10.0
Precipitation on water areas	6,950,000	155,000	8.5	1.2
Total	81,661,000	12,557,500	100.0	100.0

*Excludes industrial wastes that discharge to municipal systems. Table does not include contributions from aquatic nitrogen fixation, waterfowl, chemical deicers and wetland drainage.

CHAPTER II

SURVEY OF THE LITERATURE

Various Methods of Phosphorus Analysis

Classical methods for the determination of phosphorus in water requires substantial time and effort. Moreover, the large diversity of analytical instrumentation and increasing interest in quantifying phosphorus content in water has led to the development of many direct and indirect methods of analysis (Table II).

Phosphorus may exist in natural waters as inorganic phosphates (ortho-, meta-, or polyphosphates) or in organic combination. These compounds may be present in soluble or insoluble forms. Figure 2 shows a typical analytical scheme which is frequently used for the differentiation between these various forms of phosphorus. The scheme converts the various fractions of phosphorus to orthophosphate (4).

The most common analytical method of phosphorus determination is based on the colorimetric determination of the phosphomolybdenum complex. Orthophosphate reacts with ammonium molybdate in acid medium to form phosphomolybdic acid which when reduced yields a blue complex. The sensitivity of the test is largely dependent on the reduction step. Reduction with stannous chloride is considered the most sensitive and the best suited method for the lower ranges of phosphates usually encountered (1).

Commercially available automatic analyzers for on-site monitoring

TABLE II

CLASSICAL METHODS USED IN THE DETERMINATION OF PHOSPHORUS

Method	Comments	Reference
Phosphomolybdate	Official Method of the Association of Agricultural Chemists and the Environmental Protection Agency	(5)
Reduction reagent		
aminonaphtholsulfonic acid		(6)
ascorbic acid	superior precision	(7)
metal sulfite		(8)
stannous chloride	most sensitive	(9)
Molybdovanate		(10)
Malachite green - dodecamolybdatophosphoric acid	colored stable salt	(11)
Indirect colorimetric via La-chloranilate		(12)
Fluorometry	aluminum-morin and tin-flavonal systems	(13)
Indirect flame spectrophotometry		
standard addition of lead nitrate	inorganic phosphates give characteristic slope in calibration curves	(14)
elemental P preconcentrated on GLC	detection limit = 10^{-12} g P	(15)

TABLE II (Continued)

Method	Comments	Reference
Atomic absorption	monitor molybdate from decomposition of heteropoly acid	(1)
Activation analysis	gamma spectrum of W^{187} in tungsto-molybdophosphoric acid	(16)
Radiometry	monitoring W^{187} in tungstomolybdo-phosphoric acid	(17)
Gravimetric		
modified phosphomolybdate	tends to yield high results	(18)
quinolinium molybdate	recommended for international trade	(19)
magnesia	good accuracy, relatively slow	(20)
Potentiometric		
indirect polarographic	titration with uranyl solution	(21)
	titration with bismuthyl solution	(22)
	titration with bismuthyl plus EDTA	(23)
silver-silver chloride electrode	titration with silver, useful in standardizing biological solutions	(24)
pH titration	after salt to acid conversion via ion exchange	(25)

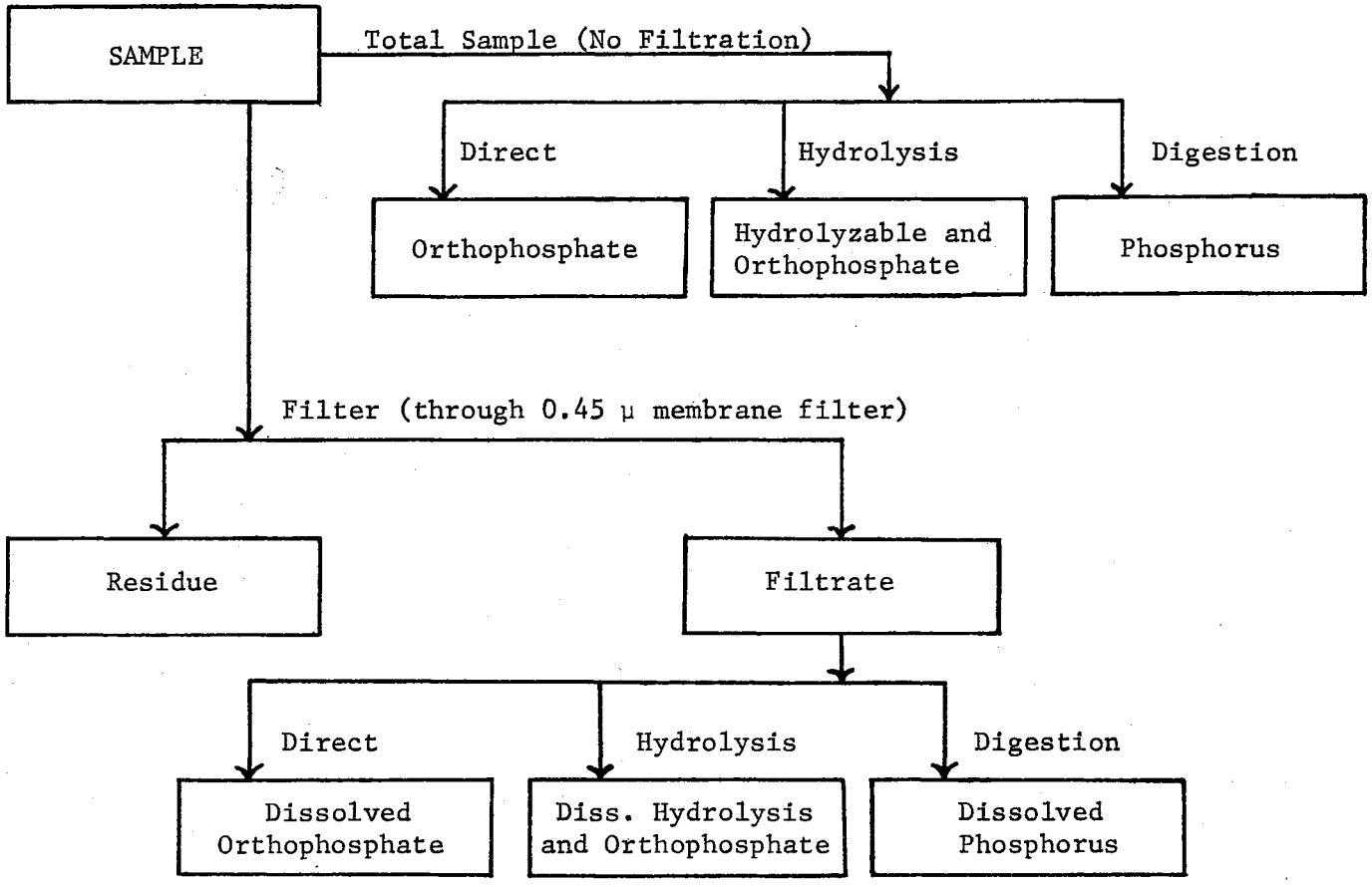

Figure 2. Analytical Scheme for Differentiation of Phosphorus Forms (4)

use the phosphomolybdate method for orthophosphate determination. Auto-analyzers, such as the Technicon CSM6 (4), use sulfuric acid as the hydrolyzing agent to obtain total inorganic phosphate. These analyzers do not include a digestion step for obtaining organic and particulate phosphorus. A consideration which limits the use of these monitors is their cost.

Current Status of Ion Selective Electrodes

Ion selective electrodes and similar sensors are found to be well suited for incorporation into continuous monitoring systems due to their relative simplicity and low cost. Table III lists electrodes most commonly used in these systems.

Electrodes of the First Class

Ion Selective Electrodes have been divided into three major classes. The first class consists of half-cells formed by metals in contact with their metal ions in solution. The resultant potential is a function of the activity of the metal ions. This relationship is expressed in the Nernst equation:

$$E = E^{o} - (0.059/n) \log a_{M^{+n}} \qquad (1)$$

Mercury and amalgam electrodes of this class have been used in the determination of standard potentials (26), activity coefficients (27), and the effect of variables such as temperature and dissolved gases (28).

Electrodes of this class can be used to indirectly measure anion concentration. For example, phosphate has been determined by titration with bismuth while monitoring with a bismuth electrode (29).

TABLE III

SELECTIVE ELECTRODES WHICH HAVE BEEN INCORPORATED INTO AUTOMATIC WATER QUALITY MONITORING SYSTEMS

Electrode	pH range	Principle interference
Bromide	0 - 14	CN^-, I^-, S^{-2}
Cadmium	1 - 14	Ag^+, Hg^{+2}, Cu^{+2}, Fe^{+2}, Pb^{+2}
Calcium	5.5 - 11	Zn^{+2}, Fe^{+2}, Pb^{+2}, Cu^{+2}, Ni^{+2}
Carbon Dioxide		
Chloride	0 - 14	Br^-, I^-, S^{-2}, CN^-, SCN^-, NH_3
Cupric	0 - 14	Ag^+, Hg^{+2}, Fe^{+2}
Cyanide	0 - 14	S^{-2}, I^-
Fluoride	0 - 8.5	OH^-
Hardness ($Ca^{+2} + Mg^{+2}$)	5.5 - 11	Zn^{+2}, Fe^{+2}, Cu^{+2}, Ni^{+2}, Ba^{+2}, Sr^{+2}
Hydrogen	0 - 14	Na^+
Iodide	0 - 14	S^{-2}, CN^-
Lead	2 - 14	Ag^+, Hg^{+2}, Cu^{+2}, Cd^{+2}, Fe^{+2}
Oxygen	0 - 14	
Nitrate	2 - 12	I^-, Br^-, S^{-2}, NO_2^-, CN^-, HCO_3^-, Cl^-, OAc^-, CO_3^{-2}, SO_3^{-2}
Sodium	0 - 14	H^+, K^+, Ag^+
Sulfide	0 - 14	

Electrodes of the Second Class

The second category contains electrodes which are formed by coating a metal with a slightly soluble salt of that metal. The half-cell potential is a function of the activity of the anions of the salt in solution:

$$E = E^{o} + (0.059/n) \log a_{A-m} \qquad (2)$$

Second Class Electrodes are commonly used as reference rather than indicator electrodes. Better known examples of this category are the calomel and silver-silver chloride electrodes.

Ito (30) has developed a silver-silver phosphate electrode for the determination of concentrated phosphoric acid at high temperatures, 200-300°C.

Montalvo and Crochet (31) developed a phosphate selective electrode composed of S.A.E. #1095 carbon steel coated with "insoluble crystalline phosphate." This was accomplished by immersion of the carbon rod in hot phosphoric acid. The resultant electrode was claimed to have a linear response from 10 to 9500 ppm phosphate and good selectivity.

Membrane Electrodes

The third type of electrodes includes all membrane electrodes. Due to a variation of physical and chemical parameters, this group is the largest and may hold vast latent possibilities in potentiometric analysis. These electrodes range from simple non-selective membranes, which develop potentials due to total ionic activity or mobility, to highly selective membranes of glass or crystal whose potential is far more sensitive to specific ions.

To be useful in an electrode, a membrane must have two properties: (i) its resistance must be sufficiently large such that it allows the development of a measurable potential between the reference and sample solutions, yet not too large for current amplification by high impedance electrometers, and (ii) the membrane should be selective to the passage of certain ions. In actual practice the later condition is only approximated.

Membrane electrodes have been divided into four sub-categories. These are solid state or crystal, solid ion exchange, liquid ion exchange, and heterogeneous membrane electrodes.

Solid State Membrane Electrodes. Electrodes of this group have a thin crystalline material as a membrane which conducts electrical current at room temperature. These membranes are mechanically stable, chemically inert, and relatively insoluble in the sample solution. Conduction through a crystal is by a lattice defect mechanism in which a mobile ion adjacent to a vacancy defect moves into the vacancy. A vacancy is fixed with respect to size, shape and charge distribution. This allows many crystals to be very selective to the ions which can be mobile within the crystal. Theory and experience have shown that only small univalent ions have sufficient mobilities to be useful in this type of electrode. This is quite advantageous in the pH and fluoride selective solid state electrode. Ross (32) describes this type of electrode and lists ten examples with their principle interferences.

Solid Ion Exchange Membranes. Eisenman (33) describes ion movement in this membrane by exchange from one relatively fixed site to another. Electrode selectivity is dependent on the relative mobilities of com-

peting ions in the membrane as well as on their ion exchange equilibrium constants.

The mobilities of the orthophosphate species are very low because of their large size and diffuse charge. Thus if a membrane of this type is to be used in a selective electrode for phosphate, more stringent requirements must be met by the exchange equilibrium constant.

Madden (29) evaluated polyvinylbenzyltrimethylammonium hydroxide as an anion exchange membrane. A linear response of 30 mV per decade change in phosphate activity was obtained. However, the membrane showed little or no selectivity.

Rohm and Guiltbault (34) has presented a preliminary report on the development of a phosphate selective membrane. This membrane electrode exhibited a good response which was non-linear. Selectivities for dibasic phosphate over univalent ions were fair. Sulfate was the only divalent anion other than dibasic phosphate to be studied. No selectivity over sulfate was found.

The electrode contained a membrane formed by the polymeric reaction of gluteraldehyde and thiourea. After silver had been complexed with this polymer, dibasic phosphate was added. A structural determination of the resulting membrane had not been attempted. The membrane may be a heterogeneous membrane containing silver phosphate or the polymer may have been phosphorylated yielding a solid ion exchanger.

Liquid Ion Exchange Membranes. These membranes differ from the solid variety in that the sites themselves are mobile. Thus the mobility and exchange equilibrium constants are primarily dependent upon the membrane solvent. Liquid ion exchangers are relatively high molecular weight organic compounds or complexes with low dielectric constant.

Their volatility and solubility in aqueous solutions are very low.

Ross (32) has described the construction and mechanism of this type of electrode, and lists eight different examples with many of their selectivity constants. The Orion Calcium Ion Electrode is the best known example of this category.

Heterogeneous Membrane Electrodes. These membranes are essentially less perfect forms of solid state membranes. Solid state material may lack the necessary mechanical properties for electrode incorporation. These properties may be controlled by dispersing an active substance in an inert matrix. The substances, successfully used to date, include ion exchange resins, sparingly soluble metal salts and chelates, and other materials which possess simple face-centered cubic crystal structure. Matrix materials include silicon rubbers, paraffin wax, collodion, polyvinyl chloride, polystyrene and polyethlene (35).

Pungor (36) reported good response to phosphate activity using a silicon rubber membrane containing manganese (III) phosphate. However, details of the electrode or its further development have not been reported. A similar electrode consisting of bismuth phosphate as the active material had been evaluated by Rechnitz (37). The electrode gave a response of 7 mV per decade change of phosphate activity. The stability was poor, drifting 1 mV in ten minutes.

CHAPTER III

THEORETICAL CONSIDERATIONS

Dependence of Phosphate Species on pH

Any aqueous solution containing phosphate must satisfy the following equilibria:

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad K_1 = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{-2} \qquad K_2 = 6.2 \times 10^{-8}$$

$$HPO_4^{-2} \rightleftarrows H^+ + PO_4^{-3} \qquad K_3 = 4.7 \times 10^{-13}$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

Control of the pH of the system circumvents the problem of these multiple equilibria. At a fixed pH, the relative ratios of the four phosphate species are constant and independent of the total amount of phosphate. The average degree of protonation of the orthophosphate species in solution, $\bar{n}$, is therefore a constant. The concentration of total phosphate may thus be written as $H_{\bar{n}}PO_4^{-3}$.

Bismuth (III) Solutions

Many phosphate salts are slightly soluble in neutral or basic solutions. However, in solutions of high acidity only bismuth phosphate is very slightly soluble. This suggests that bismuth-bismuth phosphate

might be a good metal-metal salt to be used in an electrode of the second kind.

Bismuth ions in neutral or basic solutions readily hydrolyze to form bismuth trioxide, Bi_2O_3. This precipitate persists until the pH is lowered to approximately one. As the hydrogen ion concentration approaches one-tenth molar, the precipitate dissolves forming the bismuthyl ion, BiO^+ (38). This solution is stable as long as high acidity is maintained; however, in solutions of higher pH, bismuthyl salts such as $BiO(NO_3)$ and $Bi_2O_3(OH)NO_3$ are readily precipitated (39).

Bismuth Amalgams

Bismuth amalgams have been prepared using three different techniques: electrolysis of bismuth solutions, replacement reactions of sodium amalgams on bismuth solutions, and by direct addition of bismuth metal to mercury at elevated temperatures. It has been found that amalgams with more mercury than Hg:Bi = 9:1 are liquid; those with less mercury than Hg:Bi = 2:1 are solid (40). Complexes that have been claimed to exist include HgBi, $HgBi_2$, $HgBi_3$, $HgBi_4$, $HgBi_5$, and $Hg_{38}Bi$. Apart from these, polynary alloys of even greater complexity are known to exist (41).

There are three other properties of bismuth amalgams which should be considered. The solubility of bismuth in mercury is 1.4 weight percent at 25° C. These amalgams are stable in air. And, bismuth amalgams change electrical resistance when placed in an electrical field (40).

The Bismuth Half-Cell

The half-cell reaction of the proposed electrode is

$$Bi^{o} + H_{\bar{n}}PO_4^{\bar{n}-3} = BiPO_4 + \bar{n}\, H^{+} + 3e^{-} \quad . \tag{3}$$

The half-cell potential at 25°C for Equation (3) may be written

$$E = E^{o} - \frac{0.059}{3} \log \frac{(a_{H^+})^{\bar{n}}}{(a_{H_{\bar{n}}PO_4^{\bar{n}-3}})} \quad . \tag{4}$$

At a constant pH, a_{H^+} is constant which allows Equation (4) to be written as

$$E = K + (0.059/3) \log a_{H_{\bar{n}}PO_4^{\bar{n}-3}} \quad . \tag{5}$$

The change in the potential is a function of the change in the logarithm of the activity of $H_{\bar{n}}PO_4^{\bar{n}-3}$,

$$(\partial E/\partial \log a_{H_{\bar{n}}PO_4^{\bar{n}-3}})_{pH} = \frac{0.059}{3} \quad . \tag{6}$$

At low and constant pH, the predominate phosphate anion is $H_2PO_4^{-}$,

$$[H_3PO_4] = [H_2PO_4^{-}]/k, \tag{7}$$

and the concentrations of HPO_4^{-2} and PO_4^{-3} approach zero. The analytical concentration of phosphate can now be written as a simple function of the monobasic specie:

$$[H_{\bar{n}}PO_4^{\bar{n}-3}] = k'[H_2PO_4^{-}] \quad . \tag{8}$$

Regardless of the phosphate specie(s) involved in the precipitation mechanism, the plot of emf vs the logarithm of $H_2PO_4^{-}$ activity will be equivalent to the plot of emf vs the logarithm of the total phosphate

concentration at constant pH.

Measuring the potential of the indicator electrode requires addition of another half-cell to serve as the reference electrode. This electrode must have a stable potential. Thus, for the electrode vs a reference electrode, such as the calomel, at 25°C, we have

$$E_{mv} = E_k + 19.7 \log (\text{phosphate})_{total}, \quad (9)$$

where E_{mv} is the observed potential, and E_k is the effective standard cell potential, which includes effects of junction potentials, internal resistance, and the ionic strength.

In actual practice the value of E_k is not exactly constant. Furthermore, deviation from ideal response in the indicator electrode is not uncommon, especially near the limit of sensitivity. However, through use of calibration curves, large ranges of the nonlinear response can be utilized (32).

CHAPTER IV

EXPERIMENTAL ACTIVITY

The metals used in these electrodes were Bismuth Metal Granules, Mallinckrodt Chemical Company catalog number 0220, marked 99.8 percent pure, and Bethlehem Instrument triply distilled Mercury. All chemicals used in the solutions were Baker Analyzed Reagents. Phosphate solutions were prepared by dissolving potassium dihydrogen phosphate in 0.1 M nitric acid.

Potential measurements were made on an Orion Research Digital pH-mV Meter, Model 801. Unit increments are at 0.1 mV and 0.0001 pH intervals. The temperature was manually controlled at $25^{\circ} \pm 1^{\circ}$ C.

The pH was found to vary less than one tenth of a unit around pH = 1.0.

A potassium nitrate salt bridge was constructed with tygon tubing plugged at both ends with a piece of unfired Vicor (Corning #7930). Comparative tests showed no interference from the reference electrolytes which contained chloride ions. If the test conditions required extremely small volumes of solution with the reference electrode remaining in the solution for long periods, the salt bridge was necessary.

Bismuth Amalgam Preparation

Liquid and two phase, solid-liquid, amalgams were prepared by the method of Scribner and Reilley (43). Grannular bismuth was added to

mercury in the amount necessary to prepare the desired composition. The mixture was heated for four hours at 80° C, while being stirred mechanically. The mixture was allowed to cool to room temperature, and the amalgam was washed twice with distilled water and transferred to a separatory funnel. The liquid was allowed to drain slowly into 1 N sulfuric acid, under which it was stored until needed. Amalgams of 0.5, 1.0 and an excess of 1.4 weight percent bismuth were prepared and tested.

Bismuth Amalgam Electrodes

The amalgam electrode body was a pyrex funnel with the stem bent in the shape of a U-tube. The amalgam was poured into the funnel to fill it just above the apex of the cone. Electrical contact with the voltmeter was made through a platinum wire inserted through the funnel stem. Phosphate test solutions were poured on top of the amalgam and the references electrode or salt bridge was lowered into solution. Data were recorded as soon as the potential became relatively stable. This usually required from five to twenty minutes. Deoxygenation of the solutions with nitrogen gas did not affect the stability.

After each test, the solution was removed with a suction tube. The surface of the electrode was rinsed with distilled water several times and wiped dry with a strip of filter paper.

Appendix A lists the activity coefficients used in all calculations and plots. Table IV lists typical observed potentials of replicate measurements made in random sequence. Figure 3 is a plot of these potentials vs the activity of $H_2PO_4^-$. Using various sets of data, slopes of the linear portion of similar curves were calculated by the least square method and found to be 19.7 ± 0.7 mV per decade of concentration.

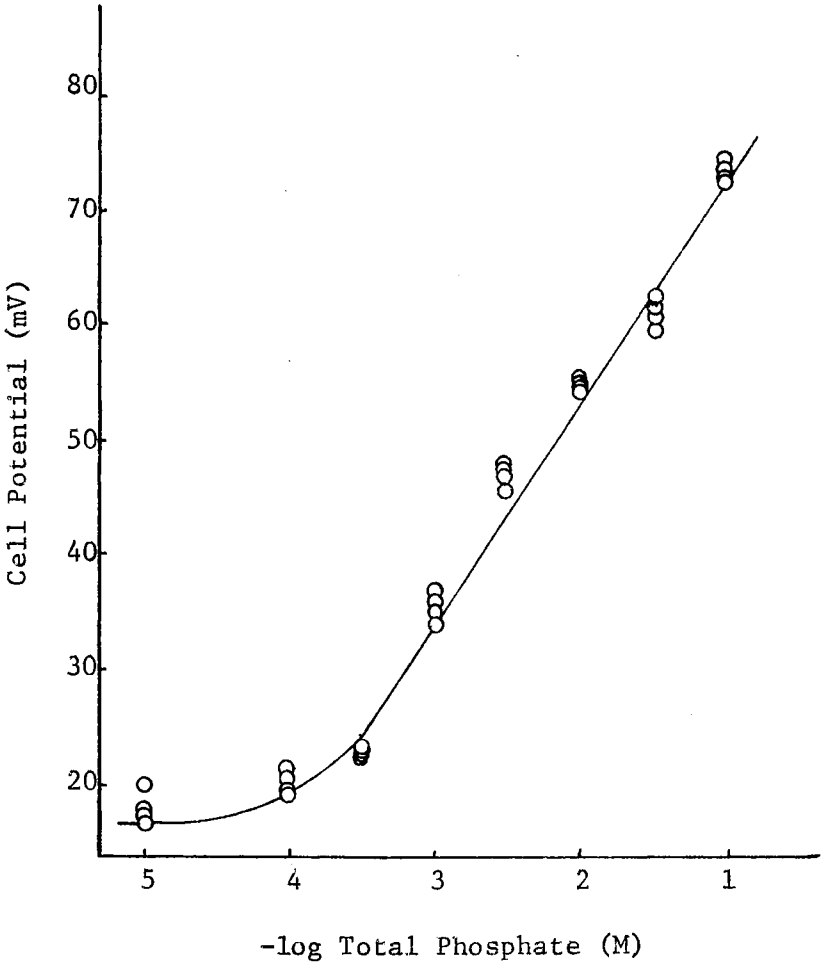

Figure 3. Calibration Curve for the Bismuth Amalgam Electrode (Four Data Points Per Concentration)

This is in accord with the theoretical value predicted by Equation (9). Frequent calibration of the electrode became necessary since the potentials were drifted as much as 7 mV over a twelve hour period.

TABLE IV

RESPONSE OF BISMUTH AMALGAM ELECTRODE TO CHANGES IN PHOSPHATE CONCENTRATION

Total Phosphate Concentration (molarity)	Electrode Response (in mV)	Average Response (in mV)
1×10^{-5}	18.4, 20.6, 18.0, 16.7	18.4
1×10^{-4}	20.3, 20.6, 21.3, 19.3	20.4
3×10^{-4}	23.2, 22.9, 23.5, 22.8	23.1
1×10^{-3}	36.5, 34.2, 35.2, 38.8	36.2
3×10^{-3}	48.4, 46.6, 45.8, 46.9	46.9
1×10^{-2}	54.7, 55.4, 54.6, 55.6	55.1
3×10^{-2}	59.0, 61.5, 58.7, 60.7	60.0
1×10^{-1}	75.0, 73.9, 74.5, 74.0	74.4

During a test, the surface of the electrode became coated with a white film. Several of these films were collected; subsequent qualitative analyses were positive for bismuth and phosphate. This strongly suggests that the electrode is of the Second Class.

Interferences

In considering possible interferring ions, attention was given to the experimental procedure used to gather data on which to base the calculations of selectivity ratios. Unfortunately, there is little agree-

ment in the literature regarding the optimal methods of determining selectivities in general or for a specified electrode. This difficulty is due to a small number of systematic studies and the tendency to report under a single, and often arbitrary, set of conditions.

The selectivity ratios in this study are based on two accepted methods. One determines the ratio of primary ion activity to interfering ion activity required to yield the same cell emf under otherwise identical conditions (44). The second, more practical analytical situation, determines the effect on the cell potential when both or perhaps many ions are present which must be estimated or determined. The mathematical derivation of the selectivity ratios for both methods are shown in Appendix B.

Table V lists the emfs of potentially interferring ions and their selectivities. These potentials vs their molar activities are plotted in Figure 4.

Metaperiodate was originally throught likely to show substantial interference. However, in acidic solutions metaperiodate is readily converted to the only slightly soluble paraperiodate form (39). Initial tests of solutions of this salt at pH 1 showed very unstable negative potentials, yielded a white precipitate while in contact with the amalgam, and were therefore not graphed.

Iodate solutions greater in concentration than 10^{-4} M exhibited similar behavior to the paraperiodate solutions and were therefore not graphed.

Table VI shows a comparison of selectivity coefficients for chloride using the two methods previously mentioned.

TABLE V

SELECTIVITY COEFFICIENTS OF SOME INTERFERRING IONS

$[H_2PO_4^-]$	mV	$a_1 = a_{H_2PO_4^-}$	Ion 2	[Ion 2]	a_2	K
10^{-2}	72.5	9.28×10^{-3}	HSO_4^-	1.3×10^{-2}	1.2×10^{-2}	7.7×10^{-1}
10^{-2}	72.5	9.28×10^{-3}	Cl^-	4.0×10^{-2}	3.5×10^{-2}	2.7×10^{-1}
10^{-3}	54.5	9.75×10^{-4}	HSO_4^-	7.0×10^{-3}	6.0×10^{-3}	1.6×10^{-1}
10^{-3}	54.5	9.75×10^{-4}	Cl^-	1.8×10^{-2}	1.6×10^{-2}	6.1×10^{-2}
10^{-4}	36.5	9.88×10^{-5}	$H_2AsO_4^-$	1.5×10^{-4}	1.5×10^{-4}	6.7×10^{-1}
10^{-4}	36.5	9.88×10^{-5}	HSO_4^-	4.6×10^{-4}	4.5×10^{-4}	2.2×10^{-1}
10^{-4}	36.5	9.88×10^{-5}	Cl^-	7.6×10^{-3}	7.1×10^{-3}	1.4×10^{-2}
10^{-4}	36.5	9.88×10^{-5}	SCN^-	3.5×10^{-2}	3.3×10^{-2}	3.1×10^{-3}

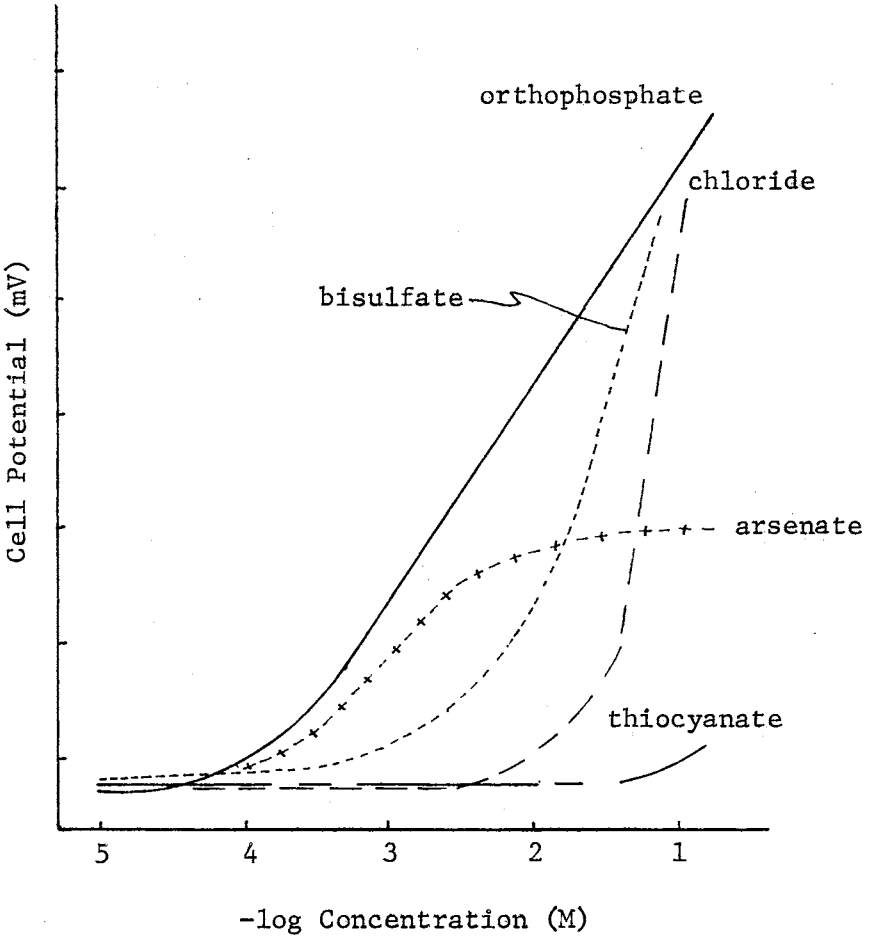

Figure 4. Comparison of Potential Response of the Bismuth Amalgam Electrode and All Ions Found to Interfere.

TABLE VI

COMPARISON OF SELECTIVITY COEFFICIENTS FOR PHOSPHATE IONS OVER CHLORIDE IONS USING TWO DIFFERENT METHODS

$a_{H_2PO_4^-}$	a_{Cl^-}	Method I $K_{single\ ion}$	Method II $K_{mixture}$
9.28×10^{-3}	3.5×10^{-2}	2.7×10^{-1}	1.9×10^{-1}
9.75×10^{-4}	1.6×10^{-2}	6.1×10^{-2}	5.3×10^{-2}
9.88×10^{-5}	7.1×10^{-3}	1.4×10^{-2}	1.0×10^{-2}

pH Titrations

Figure 5 shows a plot of the change in potential as 300 ml of phosphate solution was titrated with a potassium hydroxide solution. The concentration of the potassium hydroxide titrant was chosen to be 0.1 M to maintain a constant ionic strength during the titration. Figure 6 is a plot of the volume of potassium hydroxide solution vs pH for these titrations.

Dropping Bismuth Amalgam Electrodes

Various configurations of dropping amalgam electrodes were investigated in an attempt to improve the stability of the amalgam electrode. The apparatus consisted of a mechanically adjusted amalgam head and a capillary tubing having an inside diameter of 1/32 of an inch. This yielded very fast drop rates, unstable and irreproducible potentials. After 20 minutes of use, the capillary was partially clogged and a drop rate of 1 drop per 2 minutes resulted. At the time a 10^{-2} M phosphate solution was being tested. As the drop grew on the end of the capillary

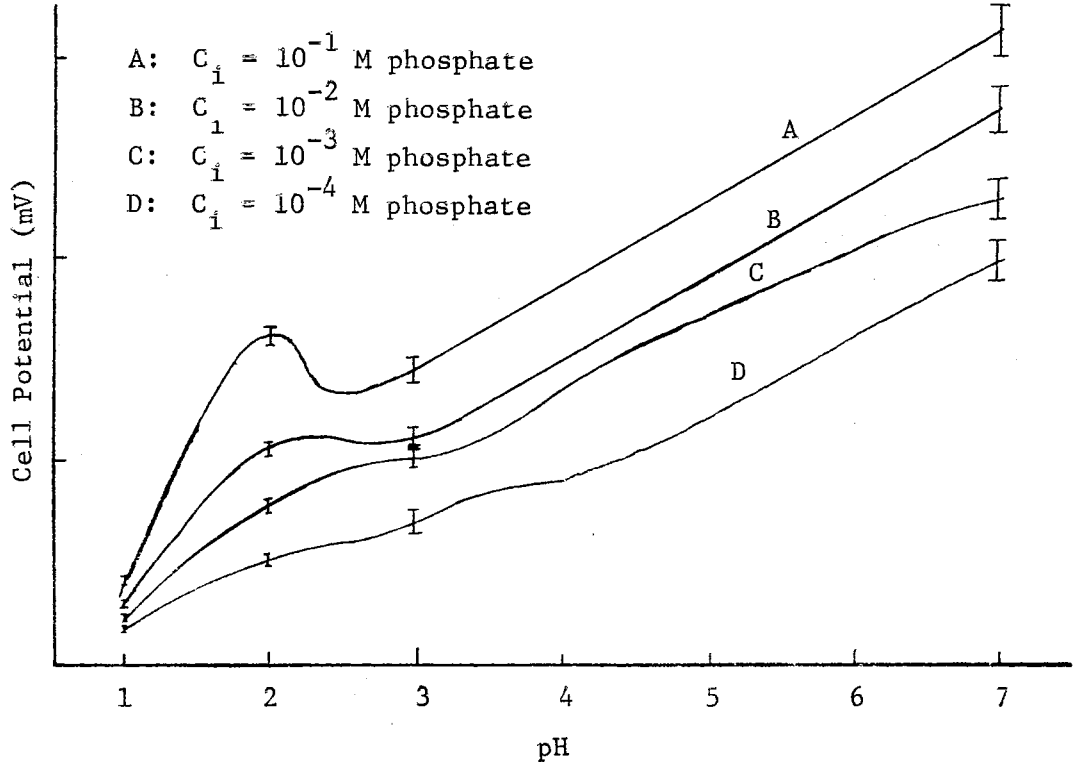

Figure 5. Potential Response of the Bismuth Amalgam Electrode to Change in pH During the Titration of Phosphate Solutions With 0.1 M Potassium Hydroxide

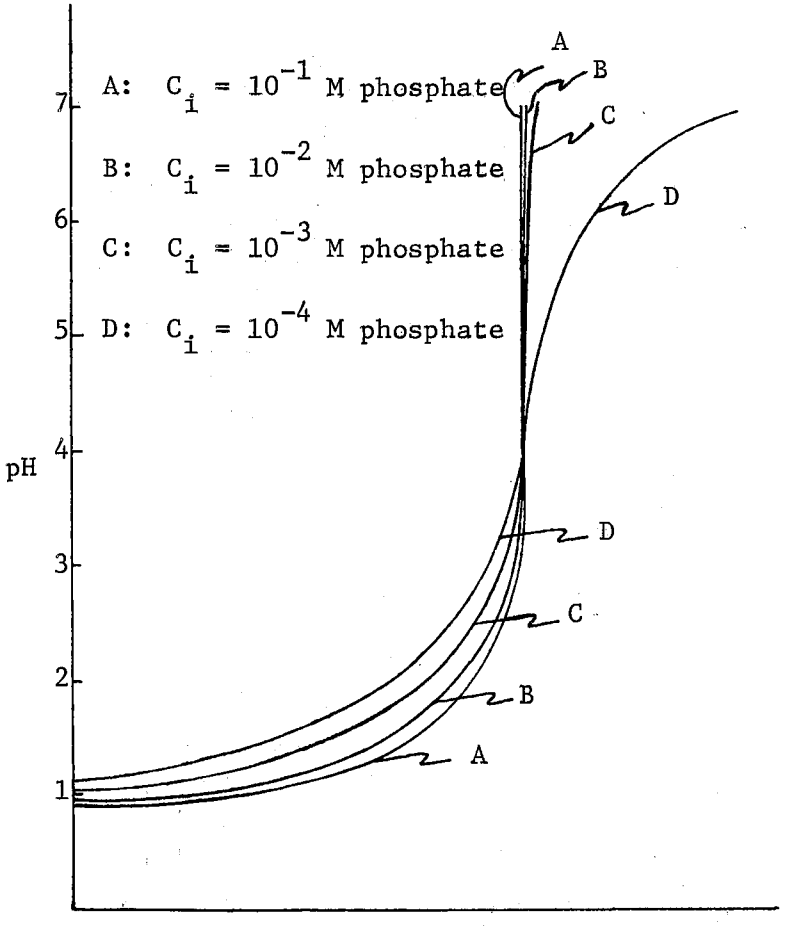

Figure 6. Titration of Phosphate Solutions With 0.1 M Potassium Hydroxide

the potential appeared to asymptotically approach 92 mV. This trend in the potential was observed for about 10 minutes. Finally, an attempt was made to change the sample solution. During careful manipulation of the solutions, the clog was freed. While unintentional clogging became a serious problem, a clog giving similar slow flow rate and potential was not observed. Usually, flow was completely stopped. Clogging and drop rate were therefore approached as two separate problems.

Hydroflouric acid was poured through a tube containing a glass frit increasing the pore size of the frit until the frit would allow passage of the liquid portion of the amalgam while filtering most of the solid-phase amalgam. Although this filter did not prevent capillary clogging, it did reduce the clogging frequency for a short while. Finally clogging of the frit was effected. Cleaning the frit proved impractical. Equally effective filtering was accomplished by a plug of glass wool in the Tygon tubing leading to the capillary.

Rate of flow through a capillary at constant conditions is controlled by the diameter and length of the capillary, and the viscosity of the liquid. Viscosity of the amalgam is fixed and the length of the capillary is limited by practicality. A short piece of marine barometer capillary tubing, approximate I.D. = 3/1000 inch, gave a drop rate of 1 drop per 10-15 seconds. No improvement in the potential was noted.

The slowest flow rate was accomplished by inverting the capillary. Amalgam entered the test solution by being forced up the tubing. It subsequently beaded and finally flowed away from the capillary. Positive pressure was applied to the amalgam reservoir by leaking nitrogen gas through a micrometer. A reproducible flow rate of 1 drop per 2 minutes was obtained by using capillary tubing with a large inside diameter. This

also decreased the clogging frequency, however, no improvement in emf stability could be observed.

Amalgamated Bismuth Billet Electrode

Madden (29) found that a bismuth billet electrode gave an irreproducible response to phosphate activity. This electrode was used successfully in monitoring titrations of pure phosphate solutions. The irreproducibility of the response at a given phosphate concentration and pH was attributed to the surface characteristics of the billet.

In the present study a similar electrode, Figure 7, was prepared. In an attempt to minimize the internal stress of the billet, the molten bismuth was allowed to cool in a temperature controlled oven after casting. The active end of the billet was made planar by resting on a porcelain plate during casting. This formed a flat surface which revealed small air pockets upon microscopic investigation. To remove these pockets and any oxide that might have formed during casting, this billet was machined and buffed with crockus cloth. The resultant surface was shiny and regular.

Modification of the billet was effected in an attempt to obtain a more reproducible active surface. After cleaning the billet with acetone, mercury was electrolytically deposited on the electrode from a 0.1 M mercurous nitrate solution. The liquid mercury dissolved into the bismuth leaving an unsmooth grey surface.

This electrode exhibited an unstable and poor potential response (approximately 5 mV per decade change in phosphate concentration). A thin white film, believed to be $BiPO_4$, formed on the active end of the electrode. This film was removed and further mercury deposition was

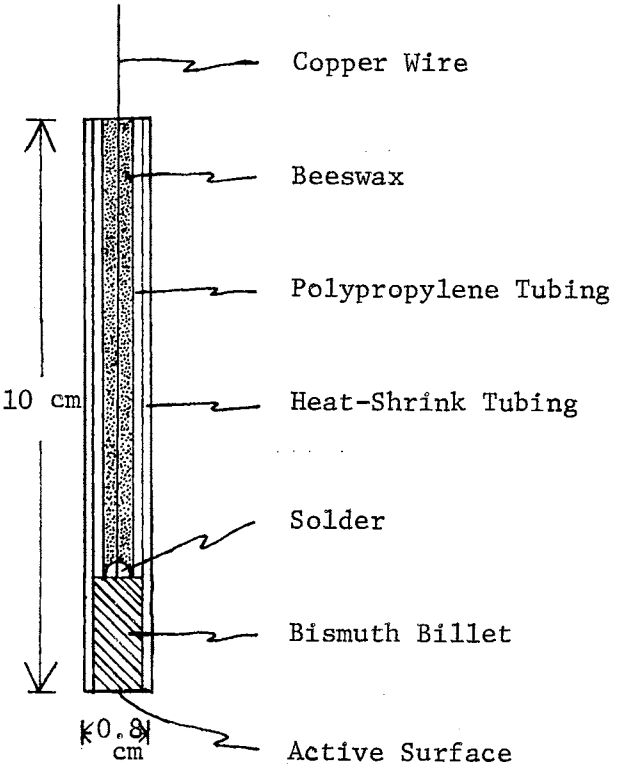

Figure 7. Structural Details of the Bismuth Billet Electrode

attempted. The mechanical integrity of the electrode decreased with the appearance of cracks in the active surface of the billet.

CHAPTER V

DISCUSSION

As enumerated in Chapter II, attempts to develop an ion selective membrane electrode for phosphate have had very little success. The membrane electrodes which are responsive to changes in phosphate concentration, show little or no selectivity to phosphate over other ions. The selectivities of membrane electrodes are primarily dependent upon the relative mobility of the ions in the membranes. The diffuse charge and large size of the phosphate species result in low mobilities for phosphate in the membranes.

Ross (32) theorizes that only small univalent ions can have sufficient mobility in a crystal lattice to be useful in membrane electrodes.

Bismuth Amalgam Electrode

The procedure described by Scribner and Reilley (43) for preparing amalgams is straightforward and proved satisfactory. Variation in amalgam composition between 0.5 and 1.4 weight percent bismuth does not influence the potential of the electrode.

Electrode Response

The bismuth amalgam electrode exhibits a response to phosphate which is linear over approximately a 4 decade range of phosphate concentration. The slope of the linear portion of the calibration curves is in excellent

agreement withthe theoretically predicted value of the Nernst equation,

$$E_{mV} = E_k + RT/nF \log (\text{phosphate})_{total}, \quad (10)$$

$$\text{or, at } 25^{\circ}C \quad E_{mV} = E_k + 19.7 \log (\text{phosphate})_{total}, \quad (11)$$

where E_{mV} is the observed cell potential and E_k is the effective standard cell potential, which includes effects of junction potentials, internal resistance, and the ionic strength. The numerical value of the slope is determined by the gas constant, R, the absolute temperature, T, Faraday's constant, F, and the number of moles of electrons transferred in the indicator electrode, n.

Accuracy

The expected relative error, RE, in the concentration due to the error in the potential, ΔE, can be seen in the first derivative of Equation (10) with respect to concentration (45): at 25° C,

$$\Delta E_{mV} = (0.2568/n)(100\ \Delta C/C) \quad (12)$$

$$\text{or, } \Delta E_{mV} = (0.2568/n)(RE). \quad (13)$$

Therefore, the relative error in concentration is independent of the concentration range or the size of the sample in which the potential is being measured. Rather, at constant temperature the relative error is directly proportional to n and the error in the measured potential.

Since the bismuth amalgam electrode undergoes a 3 electron change, the relative error in concentration is 11.7 percent per mV error in the potential.

Selectivity

A comparison of the selectivity coefficients for phosphate ions over chloride ions using two different methods is made in Table VI. The calculations of Method II, using potentials measured in solutions containing orthophosphate and chloride ions, gave selectivity coefficients smaller than those of Method I. This implies that the selectivity coefficients listed in Table V are slightly larger than those which would be encountered in practical analytical situations.

pH Titrations

Titrations of the orthophosphate solutions (Figures 5 and 6) showed several important points. While the volume of titrant (0.1 M potassium hydroxide) required to produce a specific pH was very reproducible, the potential at the new pH became less reproducible as the new pH increased. The slope of the curve for each phosphate concentration is greatest around a pH of one. Control of pH is therefore more critical in this area. Deviations from linearity occur above pH = 2. This is especially true around the pK_1 of phosphoric acid (pK_1 = 2.125) where a decrease in the potential is observed. The decrease is more pronounced in the greater concentrations of phosphate. The overall trend can be attributed to not only the multiple equilibria of the phosphate species, but also to the competition of the hydroxide ions for the bismuthyl ions.

Dropping Bismuth Amalgam Electrodes

The problems of reproducible drop rates and capillary clogging can be explained by the surface properties of bismuth and mercury. Bismuth is a glass wetting metal and mercury is a glass non-wetting metal. After

the apparatus had been used for several weeks, a film could be seen on the tygon tubing leading from the amalgam reservoir to the glass tubing. This film is believed to be bismuth metal and was probably being deposited on the walls of the capillary tubing as well.

Amalgamated Bismuth Billet Electrode

Madden (29) attributed the potential irreproducibility of the bismuth billet electrode to its surface characteristics. During the present investigation mercury was electrolytically deposited on such an electrode, Figure 7. This resulted in a lack of improvement in the potential reproducibility and a decrease in the change of emf for a given change in phosphate concentration.

Summary

The formation of a $BiPO_4$ film on the amalgam suggests that the bismuth amalgam electrode is performing as an electrode of the Second Class. The electrode gives a Nernstian slope of 19.7 mV/pC_{PO_4} from 3×10^{-4} to 1×10^{-1} M phosphate concentration. The test solutions must have a pH of one due to the competition of the hydroxide ions for the bismuthyl ions in more basic solutions. The bismuth amalgam electrode has selectivity over interferring ions (Tables V and VI) which is better than other phosphate selective electrodes described in the literature. However, in comparison to the selectivities of other electrodes for other ions, the selectivities of the bismuth amalgam electrode can only be considered fair.

The dropping bismuth amalgam configuration and the amalgamated bismuth billet electrode are unsuited for the direct determination of

phosphate due to their irreproducible potentials for given concentrations, but may be suited for titration analysis.

SELECTED BIBLIOGRAPHY

(1) Mancy, Khlil H., "Analytical Problems in Water Pollution Control," Analytical Chemistry: Key to Progress on National Problems. Eds., W. Wayne Minke and John K. Taylor. Washington: National Bureau of Standards Number 351, 1972.

(2) McGauhey, P. H., Engineering Management of Water Quality, New York: McGraw-Hill, 1968.

(3) Hasler, Arthur D., Bio. Sci., Vol. 19, (1965) 425.

(4) Dominick, David D., Ed., Methods for Chemical Analysis of Water and Waste, Ohio: Environmental Protection Agency, 1971.

(5) Harwitz, William. Official Methods of Analysis. Washington: The Association of Official Agricultural Chemists, 1955.

(6) Blaisdell, D. R., B. Compton and J. H. Nair, III, 3rd Technicon Symp., 1967: Automat. Anal. Chem., Vol. 1, (1968) 393.

(7) Henriksen, A., Vatten, Vol. 27, (1971) 44; C. A., Vol. 76, (1972), 44.

(8) Jarabin, A., M. Vajda and P. Szarvas, Acta Phys. Chim. Debrecina, Vols. 15/16, (1970) 201; C. A., Vol. 75, (1971) 25090r.

(9) Piton, B. and B. Voituriez, Cah. Oceanogr., Vol. 20, (1968) 761; C. A., Vol. 71 (1969) 40568t.

(10) Hirata, A. A. and D. Appleton, Anal. Chem., Vol. 31 (1959) 2097.

(11) Altmann, H. J., E. Fuerstenau, A. Gielewski and L. Scholz, Fresenius' Z. Anal. Chem., Vol. 256 (1971) 274; C. A., Vol. 76, (1972) 6549b.

(12) Hayashi, K. T. Danguka and K. Ueno, Talenta, Vol. 4 (1960) 244.

(13) Guyon, J. C. and W. D. Shults, J. Amer. Water Works Assoc., Vol. 61, (1969) 403.

(14) Sakai, S. and R. Okura, Kogyo Yosui, Vol. 1966 (1967) 30; C. A., Vol. 69, (1968) 6143r.

(15) Addison, R. F. and R. C. Ackman, J. Chromatog., Vol. 47 (1970) 421.

(16) Allen, H. E. and R. B. Hahn, Environ. Sci. Technol., Vol. 3 (1969) 844.

(17) Hahn, R. B. and T. M. Schmitt, Anal. Chem., Vol. 41 (1969) 359.

(18) Wilson, C. L. and D. W. Wilson. Comprehensive Analytical Chemistry, Vol. 1, New York: Elsevier, 1960.

(19) Campen, W. A. C. and A. M. J. Sledsens, Analyst, Vol. 86 (1961) 467.

(20) Graham, H. G., Jr., and T. C. McRight, J. of Agri. and Food Chem., Vol. 12 (1964) 140.

(21) Rozanski, L., Chem. Anal. (Warsaw), Vol. 17 (1972) 55; C. A., Vol. 77 (1972) 13604q.

(22) Dono, T. and G. Nakagawa, Japan Analyst, Vol. 9 (1960) 96.

(23) Haas, A. Quoted by Schall, E. D., Anal. Chem., 58R (1963).

(24) McColl, C. H. and T. A. O'Donnell, Anal. Chem., Vol. 36 (1964) 848.

(25) Madden, Marion L. "A Study of the Rapid Determination of Phosphorous in Commercial Fertilizer" (unpub. M.S. thesis, Memphis State University, 1965).

(26) Mussini, T. and A. Pagella, J. Chem. Eng. Data, Vol. 16 (1971) 49.

(27) Downes, C. J., J. Chem. Eng. Data, Vol. 15 (1970) 444.

(28) Zebreva, A. I., G. K. Efremova and M. T. Kozlovskii, Dokl. Akad. Nauk SSSR, Vol. 193 (1970) 1326.

(29) Madden, Marion L., "The Potentiometric Determination of Phosphate" (unpub. Ph.D. thesis, Oklahoma State University, 1972).

(30) Ito, K. Nakane, S. Kondo and T. Yamada, Naquoya Kogyo Daigaku Gakuho, Vol. 21, (1969) 421.

(31) Montalvo, Joseph G., Jr., and Keerney L. Crochet, "Solid State Phosphate Ion Selective Electrode." 28th Southwest Regional Meeting of the American Chemical Society, Baton Rouge Section, Baton Rouge, Louisiana, December, 1972.

(32) Ross, James W., Jr., "Solid-State and Liquid Membrane Ion Selective Electrodes." Ion Selective Electrodes. Ed., R. A. Durst. Washington: National Bureau of Standards, 1969.

(33) Eiseman, George, "Theory of Membrane Electrode Potentials." Ion Selective Electrodes. Ed., R. A. Durst. Washington: National Bureau of Standards, 1969.

(34) Guilbault, G. G. and T. J. Rohm, "Ion Selective Electrodes for Phosphate, Nitrate and Perchlorate Ions." Electrochemical and Spectrochemical Symposia, Division of Analytical Chemistry, 165th National Meeting of the American Chemical Society, Dallas, Texas, April, 1973.

(35) Covington, Arthur K. "Heterogeneous Membrane, Electrodes." Ion Selective Electrodes. Ed. R. A. Durst. Washington: National Bureau of Standards, 1969.

(36) Pungor, E., J. Havas and K. Toth, Z. Chem., Vol. 5, (1965) 9.

(37) Rechnitz, G. A., et al., Anal. Lett., Vol. 1 (1967) 29.

(38) Moeller, Therald. Inorganic Chemistry. New York: John Wiley, 1952.

(39) Cotton, F. A. and G. Wilkinson. Advanced Inorganic Chemistry, 2nd ed., New York: John Wiley, 1966.

(40) Mellor, J. W., A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. IX. London: Longmans, Green and Co., 1929.

(41) Wilkinson, M. C., "The Surface Properties of Mercury," Chemical Reviews, Vol. 72 (1972) 575.

(42) Srinivason, K. and G. A. Rechnitz, Anal. Chem., Vol. 41 (1969) 1203.

(43) Scribner, William G. and Charles N. Reilley, Anal. Chem., Vol. 30 (1958) 1452.

(44) Rechnitz, G. A., M. R. Kresz and S. B. Zamochnick, Anal. Chem., Vol. 38 (1966) 973.

(45) Light, Truman S., "Industrial Analysis and Control With Ion Selective Electrodes." Ion Selective Electrodes. Ed., R. A. Durst. Washington: National Bureau of Standards, 1969.

(46) Kielland, Jacob, J. A. C. S., Vol. 59 (1937) 1679.

(47) Butler, James N., Ionic Equilibrium. Massachusetts: Addison-Wiley, 1964.

(48) Srinivasan, K. and G. A. Rechnitz, Anal. Chem., Vol. 41 (1969) 1203.

APPENDIX A

ACTIVITY COEFFICIENTS USED IN THE CALCULATION OF MOLAR ACTIVITIES AND SELECTIVITY COEFFICIENTS

The relationship between activity, a_i, and concentration, C_i, of the ion, i, is given by:

$$a_i = \gamma_i \times C_i, \tag{1}$$

where γ_i is the activity coefficient of the ion.

In this investigation, the activity coefficients of various ions were obtained from two sources. The activity coefficients for ions at several concentrations between 1×10^{-3} and 1×10^{-1} M were obtained from Reference 46 and are listed in Table VII. All other activity coefficients were obtained from the extended form of the Debye-Huckel limiting law, Equation (2) (47). These values are listed in Table VIII. The coefficients which are in the concentration range of Table VII are in excellent agreement with the interpolated values from this table.

The Debye-Huckel equation states,

$$-\log \gamma_i = (A z_i^2 \sqrt{I})/(1 + B a \sqrt{I}), \tag{2}$$

where A = constant (at 25° C, A = 0.5115),

Z_i = the charge of the ion,

I = the ionic strength ($I = 1/2 \sum_i C_i z_i^2$),

TABLE VII

INDIVIDUAL ACTIVITY COEFFICIENTS OF IONS IN WATER (46)

Inorganic Ion	Concentration (in M)	Activity Coefficients
$H_2PO_4^-$	1×10^{-3}	0.975
	1×10^{-3}	0.964
$H_2AsO_4^-$	5×10^{-3}	0.947
	1×10^{-2}	0.928
IO_3^-	2×10^{-2}	0.902
	5×10^{-2}	0.86
HSO_4^-	1×10^{-1}	0.82
	2×10^{-1}	0.775
	1×10^{-3}	0.975
	2×10^{-3}	0.964
Cl^-	5×10^{-3}	0.945
	1×10^{-2}	0.925
NO_3^-	2×10^{-2}	0.899
	5×10^{-2}	0.85
	1×10^{-1}	0.805
	2×10^{-1}	0.755
	1×10^{-3}	0.975
	2×10^{-3}	0.964
	5×10^{-3}	0.946
NCS^-	1×10^{-2}	0.926
	2×10^{-2}	0.900
	5×10^{-2}	0.855
	1×10^{-1}	0.81
	2×10	0.76

TABLE VIII

INDIVIDUAL ACTIVITY COEFFICIENTS OF IONS IN WATER FROM THE DEBYE-HUCKEL LIMITING LAW (EXTENDED FORM)

Inorganic Ion	Concentration (in M)	Activity Coefficients
$H_2PO_4^-$	7×10^{-7}	0.999
	7×10^{-6}	0.997
HSO_4^-	2×10^{-5}	0.995
	7×10^{-5}	0.990
	2×10^{-4}	0.984
	5.6×10^{-7}	0.999
$H_2AsO_4^-$	5.6×10^{-6}	0.997
	5.6×10^{-5}	0.991
	5.6×10^{-4}	0.973
IO_3^-, Cl^-	1×10^{-5}	0.996
NO_3^- and SCN^-	1×10^{-4}	0.988

and, B = constant (at 25^{o} C, 10^{-8} B = 0.3291).

Equation (2) may be used to calculate activity coefficients at temperatures other than 25^{o} C, by using the appropriate values for the temperature dependant constants, A and B.

APPENDIX B

TWO METHODS USED TO CALCULATE SELECTIVITY COEFFICIENTS (48)

The potentials measured with ion selective electrodes in solutions containing the primary ion and any other ion to which the electrode responds, have been found to fit the empirical equation

$$E = E_o + 2.303\ RT/F \log (a_1 + Ka_2) \qquad (1)$$

where a_1 = activity of the primary univalent anion 1

a_2 = activity of any other univalent anion 2, to which the electrode responds

and K = selectivity ratio of anion 2 for the given electrode.

The selectivity ratio can be evaluated, using this equation, by carrying out potentiometric measurements in solutions containing mixtures of the ions of interest or by utilizing a series of solutions each containing only a single salt. Two major evaluative methods may be used.

Method I. The potential of an ion selective electrode in a solution containing only the primary univalent anion is given by

$$E_1 = E_o + 2.303\ RT/F \log a_1 . \qquad (2)$$

If the solution does not contain the primary anion but any other univalent anion with a selectivity ratio K, the potential of the electrode in such a solution can be expressed by Equation (3), obtained by substitut-

ing $a_1 = 0$ in Equation (1):

$$E_2 = E_o + 2.303\ RT/F\ \log\ (Ka_2). \tag{3}$$

If Equations (2) and (3) are combined with $E_1 = E_2$, we get

$$K = a_1/a_2, \tag{4}$$

where a_1 and a_2 are the activities of the two ions which produce the same potential when present separately.

Method II. The potentials of the electrode in solutions containing only the primary ion of interest, Equation (2), and in solutions containing both ions, Equation (1), is used in this method. Combining these two equations, one obtains

$$E_1 - E = 2.303\ RT/F\ \log \frac{a_1 + Ka_2}{a_1} \tag{5}$$

which can be rearranged to give an explicit expression for K,

$$K = \frac{(\exp\ \{\frac{E_1 - E}{RT/F}\})\ a_1 - a_1}{a_2}\ . \tag{6}$$

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